

Organic syntheses via transition metal complexes. LXXXI. [☆] Bis(carbene) complex of chromium connected by a conjugated ammonium pentadienide bridge

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Abstract

The reaction of pentacarbonyl(1-ethoxyethylidene)chromium and tetrachlorocyclopropene in the presence of triethylamine affords a bis(carbene) complex **3**, in which the carbene chromium units are connected by a conjugated and planar ammonium pentadienide bridge. According to NMR measurements the compound adopts a fluxional (*Z*, *E*) configuration. The structure of **3** was established by X-ray structure analysis [$C_{27}H_{27}Cr_2NO_{12} \cdot 2CH_2Cl_2$, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.703(1)$ Å, $b = 12.847(1)$ Å, $c = 13.667(2)$ Å, $\alpha = 95.77(1)^\circ$, $\beta = 110.15(1)^\circ$, $\gamma = 112.81(1)^\circ$, $Z = 2$, $R = 0.072$, $wR^2 = 0.201$].

Keywords: Chromium; Bis(carbene) complexes; Cyclopropanes; Ammonium ylide; Radialene; Bridging ligand

1. Binuclear conjugated complexes

Binuclear organometallic complexes, in which the metal centers are connected by a conjugated carbon bridge, have attracted the interest of several research groups lately with respect to a potential application as material for nonlinear optics, electrooptics and molecular electronics [2,3,4]. A wide variety of metal complexes $L_nM-(C\equiv C)_x-ML_n$ is known, in which two metal centers are connected by an alkyne bridge [5], but to date only a few examples of conjugated bis(carbene) complexes $L_nM=CX-(CR=CR)_x-XC=ML_n$ have been reported (Table 1).

2. Ammonium pentadienide bridged bis(carbene) complex

It is well established that α -hydrogen atoms of the methylcarbene chromium complex $(CO)_5Cr=C(OEt)-$

CH_3 **1** [15,16] are acidic [17] and easily replaced via enolate intermediates [18,19,20,21], e.g. by base-catalyzed condensation with aldehydes [22] or acid amides [23] to give alkenylcarbene complexes. Chain extension with cationic olefin complexes [24,25,26] and tropylium ions [27] has also been reported. An oxidative coupling in the presence of copper salts leads to formation of bridging bis(carbene) complexes [7,21,28,29,30]. Bis(carbene) complexes were also obtained by reaction of α -lithio carbene anions with diiodoalkanes [31] or by Michael addition to alkenylcarbene complexes [21].

We have generated a novel type of conjugated bridged bis(carbene) complex **3** by reacting two equivalents of **1** with tetrachlorocyclopropene in presence of triethylamine. The condensation involves the elimination of four equivalents of HCl and the formation of a hitherto unknown nitrogen ylide system, in which two carbene units are connected by an ammonium pentadienide bridge (Scheme 1).

3. Spectroscopy

The bis(carbene) compound **3** was assigned an (*E*, *Z*) configuration based on spectroscopic evidence, and on the fact that two separate signals are observed in the ^{13}C

[☆] LXXX. Paper, see [1]. Dedicated to Prof. Dr. Henri Brunner on the occasion of his 60th birthday.

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¹ Authors for correspondence relating to X-ray structure analysis.

Table 1

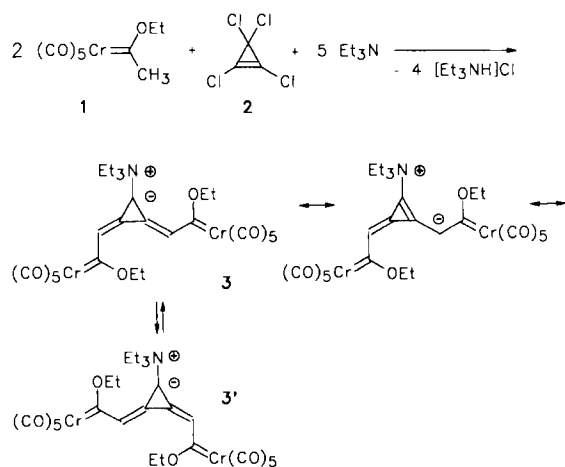
Conjugated Bis(carbene) Complexes $L_nM=CX-(CR=CR)_x-XC=ML_n$

L_nM	$=CX-(CR=CR)_x-CX=$	Ref.
$FeC_5H_5(Ph_2PCH_2PPh_2)^+$	$=CH-CH=CH-CH=$	[6]
$Mn(MeC_5H_4)(CO)_2$	$=C(OEt)-CH=CH-(OEt)C=$	[7]
$Re(Me_5C_5)(NO)(PPh_3)^+$	$=C=C=C=C=$	[8]
$Cr(CO)_5$	$=C(OEt)-CH=CH-p-C_6H_4-CH=CH-(OEt)C=$	[9]
$Cr(CO)_5$	$=C(OEt)-(biphenylene-4,4'-diyl)-(OEt)C=$	[10]
$Cr(CO)_5$	$=C(NEt_2)-CMe=C(OEt)-(biphenylene-4,4'-diyl)-(OEt)C=$ $CMe-(NEt_2)C=$	[10]
$Cr(CO)_5$	$=C(OMe)-(1,6-methano[10]annulene-2,7-diyl)-(OMe)C=$	[11]
$Mo(NAr)(OR_{F6})_2(THF)$	$=CH-CH=CH-CH=CH-CH=$	[12]
$Mo(NAr)(OR_{F6})_2(DME)$	$=CH-p-C_6H_4-CH=$	[12]
$Mo(C_5H_5)(CO)_2$	$=C(NEt_2)-(Et_2N)C=$	[13]
$W(CO)_5$	$=C(OEt)-(anthracene-9,10-diyl)-(OEt)C=$	[14]

NMR spectrum for the $Cr=C$ (δ 288.0 and 285.2) as well as for the α -CH groups (δ 130.3 and 129.8). The 1H and ^{13}C NMR signals of the exocyclic $=CH$ unit (20°C, 360 MHz, C_6D_6 solution) are dynamically broadened by a rapid (and apparently simultaneous) rotation of the exocyclic $C=C$ bonds leading to a degenerated interconversion of **3** and **3'**. A low barrier of rotation may be due to a significant resonance contribution of a polar nitrogen ylide type bond. In line with this observation is the bathochromic shift of $[\nu(C=C)] = 1700\text{ cm}^{-1}$ relative to 1780 cm^{-1} in methylene cyclopropane. More detailed structural features are revealed by the X-ray structure analysis of compound **3**.

4. Crystal structure analysis of (*E, Z*)-**3**

Fig. 1 shows the molecular structure and Tables 2 and 3 give the data of the X-ray structure analysis of (*E, Z*)-**3**. The complex forms triclinic crystals in the space group $P\bar{1}$ (No. 2). The coordination plane of the carbene carbon atom approximately bisects the angle between two *cisoid* carbonyl groups at the chromium



Scheme 1. Formation of bis(carbene) complex **3** by condensation of **1** with tetrachlorocyclopropene **2**.

atom [$C21-C22-Cr1-C41$ $138.4(5)^\circ$, $C31-C32-Cr2-C52$ $-133.2(4)^\circ$]. Both 1-metalla-1,3-diene units of (*E, Z*)-**3** adopt an *s-trans* configuration [$C2-C21-C22-Cr1$ $169.4(4)^\circ$, $C3-C31-Cr1-C41$ $-177.4(4)^\circ$], and all three exocyclic bonds of the three-membered ring are planar [sum of valence angles for $C1$ $358.7(8)^\circ$, $C2$ $359.6(4)^\circ$, $C3$ $359.9(4)^\circ$]. The conjugated diene portion exhibits an alternating CC double-bond, single-bond, double-bond sequence [$1.376(6)$ Å ($C2-C21$), $1.456(7)$ Å ($C2-C3$), $1.362(7)$ Å ($C3-C31$)] of which the $C=C$ bond distances are somewhat elongated compared to typical bond distances found in many organic conjugated diene systems [see e.g.: 1,3-butadiene, 1.330 Å ($C1-C2$), 1.455 Å ($C2-C3$)] due to delocalization of the negative charge. A strong contribution of a dipolar ylide resonance structure $Et_3N^+-C=C-CH=C(OEt)-Cr^-$ is indicated by two short [$C1-C2$ $1.350(6)$ Å and $C1-C3$ $1.370(6)$ Å] and one long bond distance [$C2-C3$ $1.456(7)$ Å] in the three-membered ring, and also by the somewhat elongated $Cr=C$ bond distances [$Cr1-C22$ $2.113(5)$ Å, $Cr2-C32$ $2.113(5)$ Å; for comparison see $(CO)_5Cr=C(OMe)Ph$ $2.03(3)$ ³²]. Based on the X-ray

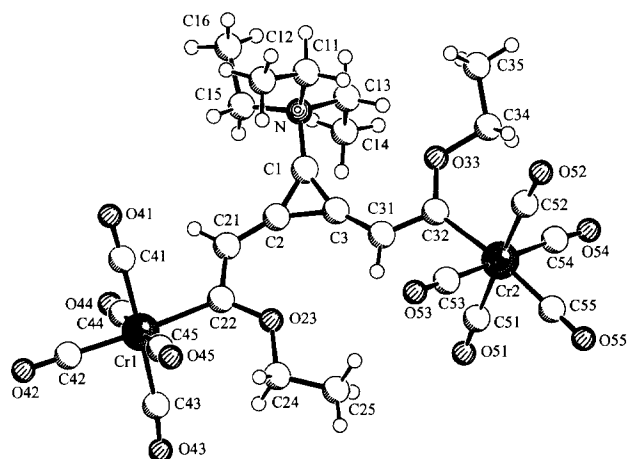


Fig. 1. Molecular structure of the ammonium pentadienide complex (*E, Z*)-**3**.

data alone, and if stressing the presence of an almost planar $\text{Cr1}=\text{C}(\text{OEt})-\text{CH}=\text{C}=\text{C}=\text{CH}-(\text{EtO})\text{C}=\text{Cr2}$ unit, compound (*E, Z*)-**3** may be considered as a butadiene-1,4-diyl bis(carbene) complex. But a more adequate bond description of the molecule is achieved by including the spectroscopic information given above. Accordingly, more attention has to be focused on the

Table 2
Selected bond lengths [\AA] and angles [$^\circ$] for bis(carbene) complex **3**

Cr(1)–C(22)	2.113(5)
Cr(2)–C(32)	2.113(5)
C(1)–C(2)	1.350(6)
C(1)–C(3)	1.370(6)
C(1)–N	1.453(5)
C(2)–C(21)	1.376(6)
C(2)–C(3)	1.456(7)
C(3)–C(31)	1.362(7)
C(21)–C(22)	1.407(6)
C(22)–O(23)	1.349(6)
O(23)–C(24)	1.443(6)
C(24)–C(25)	1.448(9)
C(31)–C(32)	1.405(7)
C(32)–O(33)	1.353(5)
O(33)–C(34)	1.434(6)
C(34)–C(35)	1.458(8)
N–C(11)	1.514(7)
N–C(15)	1.514(6)
N–C(13)	1.546(6)
C(11)–C(12)	1.512(9)
C(13)–C(14)	1.487(9)
C(15)–C(16)	1.513(7)
C(2)–C(1)–C(3)	64.7(3)
C(2)–C(1)–N	144.7(5)
C(3)–C(1)–N	149.3(4)
C(1)–C(2)–C(21)	150.4(5)
C(1)–C(2)–C(3)	58.3(3)
C(21)–C(2)–C(3)	150.9(4)
C(31)–C(3)–C(1)	157.6(4)
C(31)–C(3)–C(2)	145.3(4)
C(1)–C(3)–C(2)	57.0(3)
C(2)–C(21)–C(22)	125.5(4)
O(23)–C(22)–C(21)	110.1(4)
O(23)–C(22)–Cr(1)	129.2(3)
C(21)–C(22)–Cr(1)	120.6(3)
C(22)–O(23)–C(24)	121.5(4)
O(23)–C(24)–C(25)	109.4(5)
C(3)–C(31)–C(32)	127.9(4)
O(33)–C(32)–C(31)	110.3(4)
O(33)–C(32)–Cr(2)	130.0(3)
C(31)–C(32)–Cr(2)	119.7(3)
C(32)–O(33)–C(34)	119.7(4)
O(33)–C(34)–C(35)	110.5(5)
C(1)–N–C(11)	107.7(4)
C(1)–N–C(15)	106.5(4)
C(11)–N–C(15)	112.4(4)
C(1)–N–C(13)	108.9(4)
C(11)–N–C(13)	107.8(4)
C(11)–N–C(15)	112.4(4)
C(15)–N–C(13)	113.3(4)
C(12)–C(11)–N	114.4(5)
C(14)–C(13)–N	114.0(5)
C(16)–C(15)–N	113.7(4)

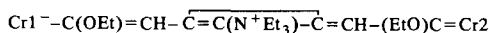
Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **3**

	x	y	z	$U(\text{eq})^a$
Cr(1)	502(1)	3452(1)	3064(1)	35(1)
C(41)	1631(7)	3245(6)	4258(6)	61(2)
O(41)	2315(6)	3143(6)	4994(5)	110(2)
C(42)	1529(5)	5057(5)	3546(5)	46(1)
O(42)	2156(4)	6056(3)	3848(4)	67(1)
C(43)	–569(5)	3715(5)	1874(5)	47(1)
O(43)	–1147(5)	3963(5)	1171(4)	74(1)
C(44)	1342(5)	3255(5)	2203(5)	47(1)
O(44)	1855(5)	3172(4)	1685(5)	74(1)
C(45)	–340(5)	3606(5)	3931(5)	44(1)
O(45)	–804(5)	3714(4)	4489(4)	62(1)
Cr(2)	–5469(1)	–3602(1)	1836(1)	37(1)
C(51)	–5547(5)	–2889(5)	680(5)	51(1)
O(51)	–5613(5)	–2488(5)	–32(4)	76(1)
C(52)	–5439(5)	–4327(5)	2981(5)	49(1)
O(52)	–5489(5)	–4748(5)	3672(4)	76(1)
C(53)	–4912(5)	–2171(5)	2856(5)	49(1)
O(53)	–4586(4)	–1332(4)	3470(5)	76(2)
C(54)	–6045(5)	–5050(5)	828(5)	48(1)
O(54)	–6452(5)	–5913(4)	203(4)	74(1)
C(55)	–7142(5)	–3951(5)	1519(5)	46(1)
O(55)	–8165(4)	–4168(4)	1332(4)	61(1)
C(1)	–408(4)	–1314(4)	2582(4)	35(1)
C(2)	–493(4)	–303(4)	2536(4)	32(1)
C(3)	–1571(4)	–1386(4)	2384(4)	32(1)
C(21)	65(4)	888(4)	2665(4)	34(1)
C(22)	–545(4)	1606(4)	2582(4)	33(1)
O(23)	–1792(3)	942(3)	2243(3)	39(1)
C(24)	–2648(5)	1458(5)	2048(6)	61(2)
C(25)	–3927(6)	536(6)	1604(7)	70(2)
C(31)	–2802(5)	–1885(4)	2215(4)	36(1)
C(32)	–3549(4)	–3041(4)	2181(4)	34(1)
O(33)	–2860(3)	–3640(3)	2377(3)	41(1)
C(34)	–3455(6)	–4861(5)	2321(6)	61(2)
C(35)	–2516(7)	–5244(6)	2857(9)	86(3)
N	453(4)	–1831(3)	2875(3)	34(1)
C(11)	581(6)	–2064(5)	3965(5)	52(1)
C(12)	1143(8)	–976(7)	4880(5)	70(2)
C(13)	–128(5)	–3023(5)	2038(5)	47(1)
C(14)	–287(6)	–2930(6)	925(5)	60(2)
C(15)	1684(4)	–948(4)	2912(5)	43(1)
C(16)	2703(6)	–1345(6)	3208(7)	69(2)
Cl(11)	2652(3)	–768(4)	590(3)	147(1)
Cl(1A)	1147(9)	459(6)	397(5)	161(4) ^b
Cl(1B)	3195(25)	1627(18)	1242(20)	382(16) ^c
C(70)	2386(13)	400(15)	247(11)	163(6)
Cl(21)	4299(4)	8304(4)	6111(4)	175(2)
Cl(2A)	6173(8)	7712(7)	6937(9)	212(6) ^d
Cl(2B)	6244(6)	7803(6)	5823(8)	123(3) ^e
C(80)	4909(12)	7372(13)	5860(9)	176(7)

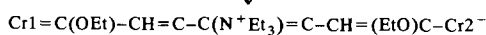
^a $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

^b SOF: 0.58(1). ^c SOF: 0.42(1). ^d SOF: 0.57(1). ^e SOF: 0.43(1).

triethylammonium pentadienide unit



†



as the most remarkable and predominant structural element of the bis(carbene) complex **3**.

5. Experimental section

All operations were performed under argon. Solvents were dried by distillation from sodium/benzophenone. ^1H NMR and ^{13}C NMR: Bruker WM 300. Multiplicities were determined by DEPT. Chemical shifts refer to $\delta_{\text{TMS}} = 0.00$ ppm. IR: Digilab FTS 45. MS: Finnigan MAT 312. Elemental analysis: Perkin-Elmer 240 Elemental Analyser. Melting points uncorrected. Column chromatography: Merck-Kieselgel 100. TLC: Merck DC-Alufohlen Kieselgel 60 F 254.

5.1. Triethylammonium-bis{[pentacarbonyl(1-ethoxyethyl-1-ylidene)chromium]-2-ylidene}cyclopropanide (3)

To pentacarbonyl(1-ethoxyethylidene)chromium **1** (256 mg, 1.00 mmol) and tetrachlorocyclopropene **2** (79 mg, 0.50 mmol) in a 5-ml screw-top vessel in 1 ml of dichloromethane is added triethylamine (253 mg, 2.5 mmol) in 2 ml of dichloromethane dropwise with vigorous stirring at -20°C . According to a TLC test compound **1** is consumed at 0°C after 20 min while a dark greenish solution is formed. 1 ml of ether and 1 ml of water is added and stirring is continued for 1 min. The mixture is centrifuged and the organic layer is separated immediately. Addition of diethyl ether affords yellow crystals of **3** (265 mg, 80%, $R_f = 0.5$ in dichloromethane, mp 100°C , dec.). ^1H NMR (CD_3COCD_3 , 20°C): δ 6.40 and 6.10 (1 H each, s dynamically broadened each, =CH each), 4.80 (4 H, s dynamically broadened, 2 OCH_2), 4.05 (6 H, q, 3 NCH_2), 1.50 and 1.42 (3 H each, s dynamically broadened each, OCH_2CH_3 each), 1.35 (9 H, t, NCH_2CH_3). ^{13}C NMR (CD_3COCD_3 , 20°C): δ 288.0 and 285.2 (Cr=C each, broad), 229.8 and 224.9 [1:4, *trans*- and *cis*-CO 2 $\text{Cr}(\text{CO})_5$], 130.3 and 129.8 (Cq each, CH=C ring each), 117.2 (Cq, N-C ring), 110.0 and 106.5 (=CH each), 78.9 (2 OCH_2), 62.7 (3 NCH_2), 21.4 (2 OCH_2CH_3), 13.4 (2 NCH_2CH_3). IR (hexane, diffuse reflection), cm^{-1} : $\nu = 2045.4$ (30), 1965.9 (5) 1900 (100) [$\nu(\text{C}\equiv\text{O})$], 1700.7 [$\nu(\text{C}=\text{C})$ exo methylene]. Anal. Calc. for $\text{C}_{27}\text{H}_{27}\text{Cr}_2\text{NO}_{12}$ (661.5): C, 49.02; H, 4.11; N, 2.12; Found: C, 49.04; H, 4.01; N, 2.14.

5.2. X-ray crystal structure

A crystal of $0.40 \times 0.35 \times 0.35$ mm was mounted on a glass fibre in inert oil (RS3000, Riedel de Haën), data were collected on an Enraf-Nonius CAD4 diffractometer with liquid nitrogen cooling at -50°C . Graphite-monochromated Mo K α radiation was used and the diffractometer was operated in ω - 2θ mode. The intensities were corrected for Lorentz and polarization effects and absorption correction was done empirically using ψ -scan-data. The structure was solved by direct methods

using SHELXS-86 and refined by full-matrix-least-squares against F^2 using the SHELXL-93 program. The figure was drawn by SCHAKAL-92. All atoms beside hydrogens were refined anisotropically, the hydrogens were placed to calculated positions and refined as riding atoms. The disordered CH_2Cl_2 -molecules were refined using geometrical restraints.

Crystal data: $\text{C}_{27}\text{H}_{27}\text{NO}_{12}\text{Cr}_2 \times 2 \text{CH}_2\text{Cl}_2$, $M = 831.35$, triclinic space group $\text{P}\bar{1}$, $a = 12.703(1)$, $b = 12.847(1)$, $c = 13.667(2)$ Å, $\alpha = 95.77(1)$, $\beta = 110.15(1)$, $\gamma = 112.81(1)^\circ$, $V = 1858.2(3)$ Å 3 , $Z = 2$, $D_c = 1.486$ g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 0.93$ mm^{-1} , $F(000) = 848$, $T = 223(2)$ K. A total of 8912 reflections were collected ($2.33 < \theta < 26.27^\circ$) of which 7492 were independent. The final R indices are $R = 0.072$ and $wR^2 = 0.201$ for 4733 observed [$I > 2\sigma(I)$] reflections and 458 refined parameters, Goodness of fit on F^2 is 1.036.

Fractional atomic coordinates and equivalent thermal parameters are given in Table 3, and selected bond lengths and angles in Table 2. Details of the X-ray crystal structure analysis are available upon request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-401866, avm. 269, names of the authors, and the journal citation.

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